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# Advanced Off-Gas Control System Design For Radioactive And Mixed Waste Treatment

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# ADVANCED OFF-GAS CONTROL SYSTEM DESIGN FOR RADIOACTIVE AND MIXED WASTE TREATMENT

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## ABSTRACT

Treatment of radioactive and mixed wastes is often required to destroy or immobilize hazardous constituents, reduce waste volume, and convert the waste to a form suitable for final disposal. These kinds of treatments usually evolve off-gas. Air emission regulations have become increasingly stringent in recent years. Mixed waste thermal treatment in the United States is now generally regulated under the Hazardous Waste Combustor (HWC) Maximum Achievable Control Technology (MACT) standards. These standards impose unprecedented requirements for operation, monitoring and control, and emissions control.

Off-gas control technologies and system designs that were satisfactorily proven in mixed waste operation prior to the implementation of new regulatory standards are in some cases no longer suitable in new mixed waste treatment system designs. Some mixed waste treatment facilities have been shut down rather than have excessively restrictive feed rate limits or facility upgrades to comply with the new standards.

New mixed waste treatment facilities in the U. S. are being designed to operate in compliance with the HWC MACT standards. Activities have been underway for the past 10 years at the INL and elsewhere to identify, develop, demonstrate, and design technologies for enabling HWC MACT compliance for mixed waste treatment facilities. Some specific off-gas control technologies and system designs have been identified and tested to show that even the stringent HWC MACT standards can be met, while minimizing treatment facility size and cost.

## INTRODUCTION

Treatment of radioactive and mixed wastes is often required to destroy or immobilize hazardous constituents, reduce waste volume, and convert the waste to a form suitable for final disposal. Thermal technologies used for mixed waste treatment include incineration, vitrification, and calcination. Lower temperature or "non-thermal" treatments that have been used or proposed for mixed waste treatment include evaporation, thermal desorption, and pyrolysis. These kinds of treatments always evolve off-gas.

Mixed and radioactive waste incineration has been used at several facilities in the U.S. and other countries (IAEA 1989, DOE 1998a). Mixed waste incineration has declined in the U.S. for several related reasons. Public opposition to incineration in general, and regulation of mixed waste thermal treatment under the new National Emission Standards for Hazardous Air Pollutants (NESHAPS) for hazardous waste combustion [Hazardous Waste Combustor (HWC) Maximum Achievable Control Technology (MACT) standards], contributed to the reassessment of existing and planned U.S. Department of Energy (DOE) mixed and radioactive waste incinerators. Two of the three DOE mixed waste incinerators, and a calciner that had been used to treat both high level and mixed wastes, that were operating at the time the HWC MACT standards were proposed and promulgated, have been closed. All of the facilities that were closed would have required either excessively restrictive feed rate limits or facility upgrades to comply with the new standards.

DOE determined to pursue alternative mixed waste treatment and disposal technologies rather than upgrade and operate those facilities to meet the new standards. These alternatives included (a) reassessing if some wastes required thermal treatment or could be otherwise equally or more safely stabilized and disposed, and (b) considering thermal and non-thermal alternatives to incineration. Regardless of whether incineration or other thermal treatment technologies were used, mixed waste treatment would generally be regulated under the HWC MACT standards unless other regulations applied, such as the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA). Even under CERCLA remediations, requirements such as the MACT standards could be applied as CERCLA Applicable or Relevant and Appropriate Requirements (ARARs).

Off-gas control technologies and system designs that have been satisfactorily proven in mixed waste operation prior to the implementation of new regulatory standards are in some cases no longer suitable. New mixed waste treatment off-gas system designs or retrofits of existing facilities, that need to comply with new regulations such as the HWC MACT standards, should consider technologies or features that can improve regulatory compliance and lower costs.

## EXISTING AND PRIOR MIXED/RADIOACTIVE WASTE THERMAL TREATMENT AND OFF-GAS CONTROL IN THE U.S.

Mixed waste treatment and off-gas systems are designed, built, and operated to comply with applicable functional, operating, and regulatory requirements. Many waste treatment and off-gas systems are summarized in IAEA 1989. More recent information on mixed/radioactive waste treatment and off-gas control systems in the U.S. is summarized in Table I. Most of the facilities listed in this table are presently closed. Only the Toxic Substances Control Act Incinerator (TSCAI), the Diversified Scientific Services, Incorporated (DSSI) mixed waste liquid-fed boiler, and the Defense Waste Processing Facility (DWPF) HLW melter are presently operational.

The design and equipment configuration for each of these systems was based on meeting treatment and air emissions requirements that prevailed at that time. For example, the Waste Experimental Reduction Facility (WERF) incinerator at the INL incinerated low-level waste (LLW) and mixed low-level waste (MLLW) for many years under Resource Conservation and Recovery Act (RCRA) Part A interim status. It met all applicable standards until the HWC MACT standards were promulgated. However, it could not comply with the HWC MACT standards for polychlorinated dioxins and furans, total $HCl/Cl_2$, and Hg, without either upgrading the off-gas system or applying excessively restrictive feedrate limits (for Cl and Hg) (INEEL 1998 and Soelberg 1999). The U.S. DOE reassessed how wastes destined for incineration in the WERF incinerator could be otherwise treated and disposed, and closed this incinerator in 2000.

While incinerators are designed to destroy primarily combustible waste feed streams, melters are designed to convert liquid, nitrate-bearing radioactive and mixed wastes into a vitrified glass to better immobilize radionuclides and hazardous metals. Melter feeds generally include not only the waste itself, which is primarily inorganic, but also glass-forming and chemically reducing additives. The glass-forming additives are necessary to provide the needed glass product composition. The chemical reductants (such as formic acid or sugar) are organic compounds that react with nitrates in the waste, mainly to increase the waste throughput through the melter. Gaseous products of the reduction-oxidation (REDOX) reactions ($N_2$, NO, $NO_2$, $CO_2$, $H_2O$, and a potential but typically unmeasured variety of incompletely reacted products such as CO and $CH_4$) are mixed with the rest of the melter off-gas (mainly evaporated $H_2O$ and sweep/inleaked air, along with entrained or volatilized particulate matter (PM)).

Off-gas systems for the different melters have included efficient wet scrubbing and dry filtration to control particulate matter and radionuclides, necessary to comply with radionuclide control requirements. Some melter off-gas systems, such as that for the West Valley Demonstration Project (WVDP), have also included $NO_x$ control to meet regulatory $NO_x$ emission limits. These off-gas systems have generally not included control of some air pollutants to levels now regulated under the HWC MACT standards. Prior to required compliance to the HWC MACT standards, these melter systems did not include oxidation of residual, incompletely oxidized organic compounds and control of mercury emissions. Currently operating mixed waste treatment facilities that are required to comply with the HWC MACT standards will require some additional off-gas control if mercury or organic materials are present in the waste feeds, or if organic reductants are added to the waste feeds.

## THE HWC MACT STANDARDS

The U.S. Environmental Protection Agency (EPA) has regulated air pollutant emissions from hazardous waste combustors based on maximum achievable control technology (MACT). The full regulation is under National Emission Standards for Hazardous Air Pollutants (NESHAP): Final Standards for Hazardous Air Pollutants for Hazardous Waste Combustors, [U. S. Code of Federal Regulations (CFR), Title 40, Part 63, Subpart EEE (Part 63 Sections 1200 through 1214)], most recently revised July 1, 2004 (EPA 2004a). The Hazardous Waste Combustor (HWC) MACT standards were promulgated in a joint effort of Resource Conservation and Recovery Act (RCRA) and the Clean Air Act (CAA) regulations, intended to consolidate and revise air emission and operational requirements previously regulated by RCRA.

The EPA first proposed the HWC MACT standards in April 1996 (EPA 1996). In the years since then, EPA has received many comments, and has revised the proposed standards many times (EPA 1997, EPA 1999, EPA 2002a, EPA 2002b). Both industry and environmental groups litigated against the final standards. Industry groups petitioned that the standards were incorrectly restrictive, based on EPA's emission database; environmental groups petitioned that the standards were not restrictive enough based on the same database. In 2001, the U.S. Court of Appeals ruled that EPA had erred in developing these MACT standards (Bastian 2002) by not appropriately using the emissions database. In response to the court ruling, EPA quickly implemented an Interim Standard Rule (ISR) (EPA 2002a). The ISR will remain in force until EPA promulgates the Phase I Final Replacement Standards and Phase II. The Phase I Final Replacement Standards and Phase II will include new, revised MACT emission standards, technical amendments not included in the ISR, and Phase II HWC MACT sources (EPA 2004b).

Existing and new incinerators, cement kilns, lightweight aggregate kilns, solid fuel-fired boilers, liquid fuel-fired boilers, and hydrochloric acid production furnaces, that use hazardous wastes, are regulated differently, with different emission limits for some species, in the Phase I Final Replacement Standards and Phase II standards. For illustration, emission limits of the

Table I. Example mixed/radioactive waste treatment and off-gas control systems in the U.S.

| Facility | Treatment system | Off-gas system | Status and comments |
|---|---|---|---|
| Waste Calcining Facility (WCF), Idaho National Laboratory (INL) (Benedict 1981) | Fluidized bed calciner, cyclone recycle, 375 L/hr (100 gal/hr) total aqueous acidic nitrated high level waste (HLW) | Cyclone, spray quench, venturi scrubber, separator, Ru adsorber, HEPAs, induced drat compressors | Started operation in 1962. Processed about 10 million liters of liquid, acidic nitrate-bearing high level waste (HLW), producing about 1,000 $m^3$ granular calcine. Closed in 1981 and replaced by the New Waste Calcining Facility (NWCF). |
| New Waste Calcining Facility (NWCF), Idaho National Laboratory (INL) | Fluidized bed calciner, cyclone recycle, 700 L/hr (180 gal/hr) aqueous acidic nitrated HLW and sodium bearing waste (SBW), which is a mixed waste | Cyclone, spray quench, venturi scrubber, separator, condenser, mist eliminator, reheater, packed bed Ru adsorber, mist eliminator, reheater, 3-stage HEPAs, 2-stage compressor, demister, reheater, HEPA | Opened in 1982. Initially used to calcine HLW. After all HLW was calcined, calcination of SBW was begun. Suspended operations in 2000 pending determinations of how to best treat and dispose the remaining SBW. If calcination is selected, compliance to the HWC MACT standards would be required, and the NWCF would require an upgrade to comply. |
| Toxic Substance Control Act (TSCA) Incinerator (TSCAI), East Tennessee Technical Park (ETTP) (DOE 1998a, Soelberg 1999) | Rotary kiln incinerator (RKI) and secondary combustion chamber (SCC), 1,100 kg/hr (2,500 lb/hr) max feedrate, solid and liquid LLW, MLLW, polychlorinated biphenyls (PCBs), sludges | Spray quench, venturi scrubber, cross-flow packed bed scrubber, 2-stage ionizing wet ESP | Opened 1991. Presently operating. By 1998, treated about 10 million kg radioactive and mixed wastes. Complies with HWC MACT standards with feedrate limits for Hg, PM, Cl, SVM, and LVM. |
| Waste Experimental Reduction Facility Incinerator (WERF), INEEL (DOE 1998a, Soelberg 1999) | Fixed hearth controlled air incinerator and SCC, 180 kg/hr (400 lb/hr) solid, sludge, and liquid LLW and MLLW | Air dilution and gas/air heat exchange cooling, pulse-jet BH, single-stage prefilter, single-stage HEPA | Opened 1985. Closed in 2000 due to combination of reduced waste feedstreams and need to upgrade (or use feedrate limits) to meet HWC MACT standards. |
| West Valley Demonstration Project (WVDP) joule heated melter. | Joule-heated, water-cooled, slurry-fed ceramic melter (SFCM) | Film cooler, submerged bed scrubber, mist eliminator, preheater, HEME, reheater, HEPA prefilters, entrainment separator, reheater, 2-stage HEPAs, positive displacement (PD) blower, reheater, $NO_x$ selective catalytic reduction (SCR) converter | Opened in 1996. Closed in 2002, after completing treatment of HLW at the WVDP (Petkus 2003). Processed nearly 24 million curies into 275 HLW glass canisters, each approximately 2,000 kg. |
| Diversified Scientific Services, Incorporated (DSSI) | Mixed liquid waste boiler, 14,000 L/day total liquid feed rate, with a single-burner, refractory-lined combustion chamber and fire-tube boiler to produce low pressure (150 lb, 1,000 kPa) saturated steam for plant heating and electricity generation | Spray dryer, pulse jet baghouse, packed bed scrubber, mist eliminator, indirect steam-heated reheater , prefilter followed by 2 HEPAs in series; scrub solution is sprayed into spray dryer so there is no liquid scrubber effluent; filter dust is stabilized to prevent metals leachability prior to final disposal | Opened 1993 after compliance demonstration. About 4.5 million kg mixed waste processed as of 2005. |
| Defense Waste Processing Facility (DWPF) at SRNL (Norton 2002, Goles 1996) | Refractory-lined, water-cooled joule-heated melter | Film cooler, dilution air, spray quench, off-gas condenser, 2-stage steam atomized scrubber (SAS), condenser, HEME, HEPA, sand filter, induced draft fan. | Opened 1996. Presently operating. As of 2002, has processed over 20% of a total 140 million liters of stored HLW, producing over 1,200 stainless steel canisters of borosilicate HLW glass. |
| Consolidated Incineration Facility Incinerator (CIF), Savannah River National Laboratory (SRNL) (DOE 1998a, Soelberg 1999) | RKI and SCC, 1,100 kg/hr (2,426 lb/hr) max feedrate, solid and liquid HW, LLW, and MLLW. | Spray quench, steam-atomized scrubber, cyclone, ME, prefilter, HEPA | Opened April 1997 for mixed waste incineration. Suspended operations in August 2000 due to combination of under-utilization (less mixed waste feedstreams compared to estimates) and determination of more cost-effective methods to treat mixed waste. |
| Transportable Vitrification System (TVS), Oak Ridge National Laboratory (ORNL) (DOE 1998b, Jantzen 2000) | Refractory-lined joule-heated melter sized for up to 300 lb/hr liquid feed rate | Spray quench, packed bed cooler, variable throat venturi, mist eliminator, reheater, and HEPAs. | Opened for mixed waste processing in June 1997, suspended operations in October 1997 after processing 7,345 kg mixed waste, produced 7,970 kg mixed waste glass. |

ISR and the proposed Phase I Final Replacement Standards for new incinerators are shown in Table II.

The EPA has included mixed waste thermal treatment facilities among facilities regulated under the HWC MACT standards because of the hazardous waste component of mixed waste. Shortly after the HWC MACT standards were proposed, the U. S. Department of Energy (DOE) Mixed Waste Focus Area provided commented to EPA that it was not appropriate or practical to regulate mixed waste treatment facilities under the HWC MACT standards (Eaton 1996, INEEL 1996, Pelletier 1997), because the radiological hazards of mixed waste, in addition to the chemical and toxic hazards associated with the hazardous waste component, make mixed wastes and mixed waste treatment facilities sufficiently unique to require other regulations than those that focus just on the hazardous waste component. The EPA considered excluding mixed wastes from the HWC MACT standards, but eventually included mixed wastes in the MACT standards promulgation.

These hazards also dictate strict control of radioactive contamination and exposure to protect workers, the public, and the environment. Regulating mixed waste thermal treatment facilities under the HWC MACT standards has created some distinct challenges for these facilities because the HWC MACT standards are in some cases incompatible with some DOE requirements, especially As Low As Reasonably Possible (ALARA) requirements.

Regulating mixed waste treatment under the MACT standards introduces incompatibilities that are not readily resolved and will require negotiation with regulators. For example, the Hanford RPP WTP recently negotiated with EPA to waive the 7% $O_2$ correction for the joule-heated melters that will be used to treat Hanford's LAW and HLW. These tank wastes are aqueous solutions that contain practically no organic content. During vitrification, they would produce essentially no combustion gas, even though organic reductants added to the melter feed to react with nitrates and nitrites in the feed will produce combustion gas ($CO_2$ and $H_2O$). The 7% $O_2$ correction is not possible when the off-gas, as in the case of Hanford's melters, is primarily purge and cooling air (Oh 2000).

## NEW MIXED WASTE THERMAL TREATMENT AND OFF-GAS CONTROL SYSTEMS IN THE U.S.

New mixed waste treatment facilities or upgrades of existing facilities have been proposed, or are presently in design and construction, to meet current waste treatment and off-gas control requirements. Examples are listed in Table III. Some of these, such as the LLW and HLW melter systems for the Hanford River Protection Project, are under construction. Others, such as the In-Container Vitrification (ICV) melter process for supplemental LAW waste treatment at Hanford, and the fluidized bed steam reformer system at INL, are in design and demonstration phases. Some other systems such as the proposed SBW Vitrification Facility, and the proposed NWCF upgrade for HWC MACT compliance, were conceptually designed, complete with equipment and facility sizing and mass and energy balances, but were eventually not selected for further design and construction.

These new or proposed mixed waste treatment facilities indicate how specific mixed wastes are being treated to meet storage and disposal requirements and how compliance to the HWC MACT standards is being accomplished for mixed waste treatment facilities. Pre-existing facilities that are continuing operation with HWC MACT compliance are doing so with feed limits or by limited modifications to enable compliance.

Regardless of primary mixed waste thermal treatment technology, MACT-compliant off-gas systems generally have these unit operations:

- Off-gas temperature adjustment – cooling to filtration/scrubbing temperatures and heating for preventing moisture condensation or for certain off-gas reaction processes such as organics oxidation or $NO_x$ reduction
- PM, radionuclide, and condensable metals removal
- Acid gas removal
- $NO_x$ control (in cases when the feed contains nitrated compounds)
- Final certified, usually redundant HEPA filtration

How these unit operations are used are defined by design and performance objectives that apply at most mixed waste treatment facilities (Peurrung 1996, Oh 2000, Anderson 2003):

- Control off-gas emissions to meet regulatory limits
- Provide continuous process and emissions monitoring
- Ensure that a nuclear criticality will be avoided
- Accept off-gas flowrate and composition variations from the primary treatment process without upsets or degradation of performance beyond acceptable limits
- Operate reliably with minimal downtime and upsets
- Comply with As Low As Reasonably Achievable (ALARA) objectives by minimizing the exposure of workers, the public, and the environment to radiological and other hazards
- Minimize amounts of secondary streams and maximize ease of secondary stream final treatment and disposal
- Minimize total treatment facility life-cycle cost
- Minimize technology implementation risk

Specific off-gas technologies, and their sequence in off-gas systems, vary depending on site-specific requirements and designer preferences for meeting the general above-listed objectives. In some cases, discriminators between specific off-gas control technologies are minor, and their selection depends more on designer preference or trade-off of lower-tier objectives. For example, some designers favor submerged bed wet scrubbers over other scrubbers (because of this technology's passive scrubbing features), where-as other designers favor high-energy or packed bed scrubbers (that also meet scrubbing objectives, with lower pressure drops, but require active scrub solution pumping).

Table II. Interim and proposed final HWC MACT emission limits.

| Pollutant/surrogate (a) | Interim Standard Rule (EPA 2004a) | Proposed Final Replacement Standard (b) (EPA 2004b) |
|---|---|---|
| Dioxin/furans, ng TEQ/dscm (c) | 0.20 | 0.11 for dry air pollution control devices (APCDs) or waste heat boilers (WHBs); 0.2 for others |
| Hg, ug/dscm | 45 | 8 |
| Particulate matter (PM), mg/dscm | 34 (0.015 gr/dscf) | 1.6 (0.00070 gr/dscf) [or an alternative to this standard (d)] |
| Semivolatile metals (SVM – Cd and Pb), ug/dscm (e) | 120 | 6.5 |
| Low volatile metals (LVM – As, Be, Cr), ug/dscm, (e) | 97 | 8.9 |
| Total $HCl/Cl_2$ as HCl, ppm (f) | 21 | 0.18 (or site-specific, risk-based emission limit based on national exposure standards) |
| Total hydrocarbon (THC) (g, h) | 10 (or 100 ppm CO) | Same |
| Destruction and Removal Efficiency (DRE) | 99.99% each POHC (i), 99.9999% for dioxin wastes | Same |

a. Some parameters are used as surrogates to indicate compliance with hazardous air pollutants. PM is used as a surrogate for non-enumerated metals Sb, Co, Mn, Ni, and Se. CO and HC are used as surrogates for organic hazardous air pollutants. DRE is used to indicate the control of organic hazardous air pollutants other than D/Fs, which are controlled by a specific standard.
b. All emission concentrations are corrected to a dry, 7% $O_2$ basis.
c. TEQ = Toxicity equivalency quotient, the international method of relating the toxicity of different dioxin/furan congeners to the toxicity of 2,3,7,8-tetrachlorinated dibenzo-p-dioxin (2,3,7,8-TCDD).
d. The 3-part alternative to the PM standard – (a) meet the SVM and LVM standards for both enumerated and non-enumerated metals not including Hg, (b) demonstrate reasonable metals feed control, and (c) demonstrate that the air pollution control system achieves at least 90% semivolatile metals removal efficiency.
e. Total metals regardless of speciation.
f. Total HCl and $Cl_2$ in HCl equivalents ($Cl_2$ in ppm is multiplied times 2 to get HCl equivalents).
g. Hourly rolling average. THC is reported as propane.
h. Facilities that choose to comply with the CO standard by continuously monitoring CO rather than HC emissions must also demonstrate compliance with the HC standard of 10 ppmv during DRE test runs performed in the comprehensive performance test.
i. POHC = Principal organic hazardous constituent.

Table III. Example mixed/radioactive waste treatment and off-gas control systems currently planned, proposed, or under construction in the U.S.

| Facility | Treatment system | Off-gas system | Status and comments |
|---|---|---|---|
| Proposed upgrade for the NWCF to meet HWC MACT standards | Fluidized bed calciner, cyclone recycle, 700 L/hr (180 gal/hr) aqueous acidic nitrated SBW | Existing: Cyclone, spray quench, venturi scrubber, separator, condenser, mist eliminator, reheater, packed bed Ru adsorber, mist eliminator, reheater, 3-stage HEPAs, 2-stage compressor, demister, reheater, HEPA<br>Proposed upgrade: HEPA filters, staged $NO_x$ and organics destruction, reheater, carbon bed Hg sorption, reheater, final HEPA and ID fan | Upgrading the existing NWCF to meet HWC MACT compliance has been studied in feasibility studies and preconceptual designs since 1997 (Rawlins 1997, Ashworth 2000, Soelberg 2003a, Barnes 2003, Merrick 2004, Barnes 2004). Upgrading the NWCF to enable continued NWCF operation with MACT compliance was eventually not selected as the preferred SBW treatment option. |
| Proposed SBW Waste Vitrification Facility at the INL | Refractory-lined joule-heated melter | Film cooler, acid quench, venturi, HEME, reheater, prefilter, HEPA, staged $NO_x$ and organics destruction, quench, ME, reheater, carbon bed Hg sorption, HEPA, ID fan | Vitrifying the SBW was one of several alternatives evaluated for treating the SBW (Quigley 2000, Bates 2001, Taylor 2001, Barnes 2004). The off-gas system was designed to be HWC MACT-compliant (Wood 2001). SBW vitrification was eventually not selected as the preferred SBW treatment option. |
| Proposed SBW steam reforming facility at the INL | Fluidized bed steam reformer system | Cyclone, oxidizing unit, partial quench, prefilter, HEPAs, carbon bed Hg sorption, ID fan | SBW steam reforming was one of several alternatives evaluated for treating the SBW (Williams 2002, Barnes 2004, Cowan 2005). Steam reforming has been selected as the preferred SBW treatment option. |
| Hanford River Protection Project (RPP) Waste Treatment Plant (WTP) HLW and LLW joule heated melters | Two separate refractory-lined joule-heated melters – 1 for HLW and 1 for LLW | Film cooler, submerged bed scrubber (SBS), wet electrostatic precipitator (WESP, with recycle back to the melter feed), high efficiency mist eliminator (HEME), (HLW melter system only), heater, 2-stage HEPAs, ID fan, carbon bed Hg sorption, Ag mordenite I sorber (HLW melter system only), gas-gas heat exchanger, heater, thermal catalytic oxidizer (TCO), 2-stage $NO_x$ selective catalytic reduction (SCR), packed bed scrubber (PBS), HEME, ID fan | Design, construction, and permitting in simultaneous progress, scheduled for startup in about 2011 or later. An off-gas system design based on high temperature filtration and staged $NO_x$/organics destruction was initially recommended (Peurrung 1996) but eventually not selected. |
| Demonstration Bulk Vitrification System (DBVS) (Hanford LAW supplemental treatment) (Raymond 2005) | ~650 kW graphite-electrode joule-heated disposable in-container melter (In-Container Vitrification, ICV); melter box designed to be final glass container | Melter hood, sintered metal high temperature filter, water scrubbing, caustic scrubbing, $NO_x$ SCR with Tri-Mer SBS for backup NOx control, HEPA filtration. | Bulk vitrification was selected over other candidate technologies in 2003. The full-scale demonstration facility, DVBS, startup is planned for late 2005. |

## OFF-GAS TECHNOLOGIES AND CONCEPTS FOR FUTURE OFF-GAS SYSTEM DESIGNS

The INL has been researching, developing, and using a variety of mixed waste treatment and off-gas control technologies and systems for decades. The INL has operated a mixed waste incinerator, a mixed waste metal melter, two fluidized bed calciners, and high level waste and mixed waste evaporators. Each of these treatment systems has included off-gas control systems. In the past decade, the INL has tested, developed, and designed advanced treatment technologies including high temperature melters, thermal desorption, and fluidized bed calcination and steam reforming technologies.

These projects have included off-gas control technology development and demonstrations in the five most challenging areas, or areas of greatest need and technical uncertainty, for mixed waste off-gas control: high temperature filtration, $NO_x$ control, organics oxidation, Hg control, and off-gas system design concepts. A few recommendations can now be made for future mixed waste off-gas system designs based on work at the INL and advances elsewhere that can provide more confidence in certain new off-gas control technologies or new applications.

### High Temperature Filtration

High temperature filtration has been in use in many applications for decades. Examples of successful high temperature filter operation in radioactive processes include the radioactive waste operations at the Forshungzentrum Karlsruhe (Karlsruhe Research Center) in Germany (Dirks 1998), and the Studsvik Radioactive Waste Fluidized Bed Steam Reforming Processing Facility in Erwin, Tennessee (Mason 1999). During the late 1990's, the DOE Mixed Waste Focus Area funded high temperature filtration demonstration projects. Most recently, high temperature filtration was included for the past 4 years of periodic demonstration tests performed by the INL for fluidized bed steam reforming (Olson 2004).

These successful operations and demonstrations of high temperature filtration provide operating data showing that high temperature filtration can be used more widely in mixed waste off-gas systems. Both sintered metal and ceramic filters have been used with success, and each have specific advantages. Sintered metal filters, such as were used in the INL steam reforming tests, are less susceptible to physical or thermal shock. Removal efficiencies for the INL filters ranged between 99.5% to over 99.9%. While ceramic filters are susceptible to breakage from physical or thermal shock, these are used successfully in the Studsvik radioactive waste steam reforming facility with removal efficiencies ranging up to 99.9%. The filters are replaced during every shutdown, by allowing the old filters to fall into the filter hopper after which they are broken up and combined with the filter ash product.

### $NO_x$ Control and Organics Oxidation

Several $NO_x$ control technologies including selective catalytic reduction (SCR), non-selective non-catalytic reduction (NSNCR), and steam reforming have been studied for mixed waste off-gas systems for many years. SCR $NO_x$ control was successfully demonstrated for the INL New Waste Calcining Facility in the 1990's, was used successfully at the West Valley Demonstration Project, and is planned for the Hanford River Protection Project melter systems. However, concerns about SCR catalyst poisoning, SCR reagent handling, process control during upset conditions, and formation of potentially explosive ammonium nitrate, have limited SCR applications and have increased process cost and complexity.

The INL has discarded SCR $NO_x$ control in favor of NSNCR, also called staged combustion. Test results and modeling (MSE 2001, Boardman 2004, Olson 2004) have provided data and confidence in the ability of NSNCR to achieve high efficiency $NO_x$ destruction (exceeding 99% under some conditions) and high efficiency destruction (exceeding 99.99% for some conditions) of residual organics in off-gas streams from melters, calciners, and steam reformers. Properly operated NSNCR systems can achieve not only highly efficient destruction of off-gas $NO_x$ resulting from processing nitrate and nitrite-bearing mixed wastes, but also can replace any other off-gas organics control technology. This combination eliminates any concerns related to SCR $NO_x$ control and can meet applicable regulatory limits for both $NO_x$ and hydrocarbon emissions and for POHC destruction efficiency.

NSNCR systems tested to date have used added fossil fuel (natural gas, propane, or fuel oil) to provide heat needed to heat the off-gas to the desired operating temperatures of 800-1,000$^o$C, and to adjust the off-gas stoichiometry in the first (de$NO_x$) stage. The added stage 1 fuel (and air, if needed) needed to heat the off-gas can cause the total off-gas flowrate to increase by 1.5 to 3 times. This increase can be eliminated by using electrical or indirect heating to heat the off-gas to the stage 1 temperature. A demonstration-scale prototype of an electrically-heated NSNCR process for destroying $NO_x$ and residual hydrocarbons from a liquid-fed cold crucible induction melter (CCIM) is shown in Figure 1.

### Mercury Control

Mercury was used in fuel reprocessing, and so is present in liquid mixed wastes from nuclear fuel reprocessing activities. Mercury control efficiencies exceeding 99.9% are required for thermally treating these wastes compliant to the HWC MACT standards. The INL has been studying and developing technologies to remove Hg from the liquid wastes, and to remove Hg from mixed waste treatment off-gas, for over a decade (Chambers 1998, Soelberg 2003b). Results show that (a) even if waste pretreatment is used to remove much of the Hg prior to thermal treatment, efficient off-gas Hg control will still be necessary for Hg-laden fuel reprocessing wastes, and (b) the only reliable and efficient technology presently available for Hg control in mixed waste off-gas systems is sulfur-impregnated activated carbon beds. Wet scrubbing, used in some non-nuclear applications, is not reliable enough or efficient enough for removing off-gas Hg regardless of speciation. Innovations such as oxidizing systems to oxidize elemental Hg to less volatile or more water-soluble species, that would enable more efficient and reliable Hg wet scrubbing, are promising, but not sufficiently demonstrated for mixed waste processes. Carbon injection, used worldwide for Hg and dioxin/furan control, is not generally efficient enough, and it generally produces up to 10 times more spent carbon waste than fixed carbon beds do.

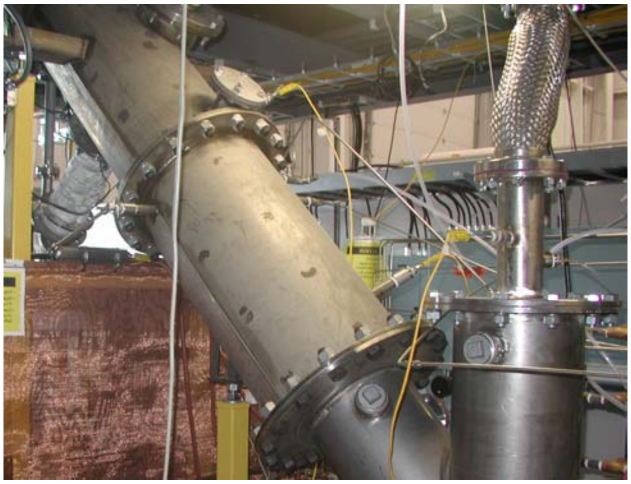

Figure 1. Demonstration-scale NSNCR reactor for CCIM $NO_x$ and hydrocarbon control at the INL. The CCIM off-gas is electrically heated, and blended with a reductant (natural gas) to convert $NO_x$ to $N_2$ in Stage 1; the hot Stage 1 gas is cooled to about 800°C in Stage 2, and blended with air to fully oxidize residual hydrocarbons in Stage 3 at temperatures under 1,200°C. The overall gas volumetric flowrate increase (from the added reductant, quench water, and combustion air) is about 1x. This increase could be reduced by 50% by using oxygen instead of air for stage 3 oxidation.

Laboratory and pilot-scale tests have shown that sulfur-impregnated carbon can sorb Hg, regardless of speciation, with high efficiencies (up to at least 99.97%) and low outlet Hg concentrations (down to below 1 ug/dscm, corrected to 7% $O_2$, dry basis) (Boardman 2004, Olson 2004, and others). These test results and design projects have determined full-scale carbon bed design and operating parameters (Soelberg 2003).

**Innovative Off-gas System Design Concepts**

Using the off-gas technologies described above, mixed waste off-gas systems can be configured that might be simpler, more reliable, have lower technical risk, and have lower costs than some current designs. For example, the off-gas system for the Hanford River Protection Project LAW melter has up to 13 different unit operations, not counting the second HEPA and the second SCR bed (Figure 2). Part of this complexity is because the hot melter gas is cooled for wet scrubbing, then reheated for filtration, then heated some more for hydrocarbon oxidation and SCR $NO_x$ destruction (and probably cooled between the two SCR stages), and cooled again for more wet scrubbing. All these unit operations cause enough pressure drop that either two ID fans are required at different locations, or a portion of the off-gas system downstream of the first ID fan will need to operate at positive pressure, not desired for contamination control in mixed waste processes.

A simpler off-gas system (Figure 2)uses NSNCR $NO_x$ and hydrocarbon control removes PM and radionuclides early in the process, and utilizes only 9 different unit operations (counting the 2-stage NSNCR reactor as 2 unit operations), while avoiding issues including (a) nitration and acidification of the SBS and WESP solutions, (b) the above-listed $NO_x$ SCR issues, (c) catalyst poisoning and destruction efficiency issues for the thermal catalytic oxidizer (TCO), and (d) carbon bed performance questions related to its placement upstream of the TCO and SCR, where elevated $NO_x$ and hydrocarbon concentrations might interfere with Hg sorption. This configuration is similar to the Option 2 recommended for the Hanford LLW vitrification process off-gas system in 1996 (Peurrung 1996). The off-gas flowrate will increase for the recommended system configuration by 1-2x due to the additions of $NO_x$ reductant, oxidizing air, and evaporated water. This increase is dwarfed in the 13-step design by a 5-10x increase caused by the film cooler air, water spray quenches, and $NO_x$ reductant addition. Some uncertainty in this new concept exists, especially regarding slagging and corrosion control in the NSNCR reactor. This might be controlled by allowing slagging and using appropriate equipment design and material selection. An even simpler alternative places the carbon bed after the 2-stage HEPA, eliminating the need for the reheater, and eliminating the potential for Hg contamination of the scrub solution. More quantitative comparisons of these different system configurations, obtained by performing equipment and footprint sizing, mass and energy balances, and cost estimates for each configuration, might confirm that the recommended options have lower costs and lower technical risk.

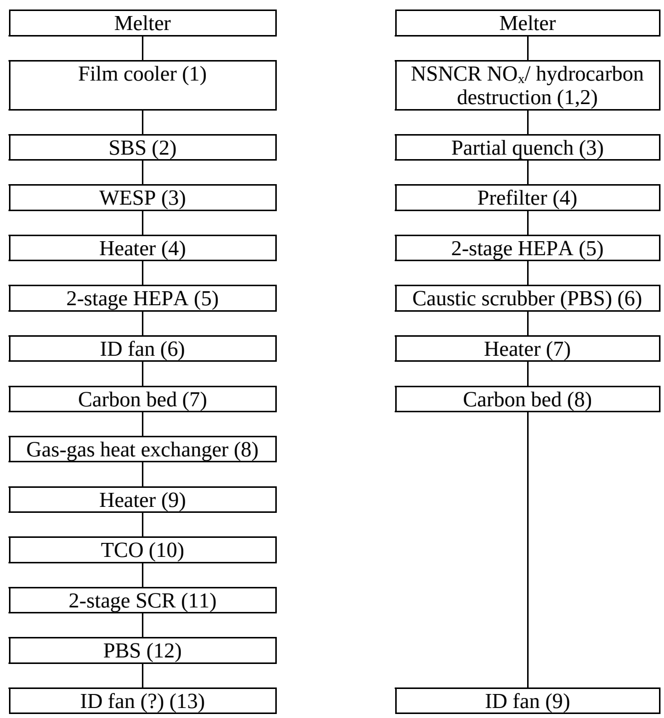


Figure 2. Joule-heated melter off-gas system alternatives.

## CONCLUSIONS AND RECOMMENDATIONS

Air emission regulations have become increasingly stringent in recent years. New mixed waste treatment facilities in the U. S. are being designed to operate in compliance with recently promulgated HWC MACT standards. Specific off-gas technologies, and their sequence in off-gas systems, vary depending on site-specific requirements and designer preferences for meeting the general above-listed objectives.

Activities have been underway for the past 10 years to identify, develop, demonstrate, and design technologies for enabling MACT compliance for mixed waste treatment facilities. Some specific off-gas control technologies and system designs have been identified and tested to show that even the stringent MACT standards can be met, while minimizing treatment facility size and cost.

Successful operations and demonstrations of high temperature filtration have provided operating data that shows that high temperature filtration can be used more widely in mixed waste off-gas systems. A range of specified removal efficiencies are available. Removal efficiencies of 99.5% to over 99.9% have been demonstrated.

Test results and modeling over several years provide performance data and confidence in the ability of NSNCR to achieve high efficiency $NO_x$ destruction (exceeding 99% under some conditions) and also high efficiency destruction (exceeding 99.99% for some conditions) of residual organics in off-gas streams from melters, calciners, and steam reformers. Using electrical or indirect heating to heat the off-gas to the stage 1 temperature can reduce the total off-gas flowrate.

Mercury is ubiquitous in liquid mixed wastes from nuclear fuel reprocessing activities. Mercury control efficiencies exceeding 99.9% are required for thermally treating these wastes compliant to the HWC MACT standards. Fixed beds of sulfur-impregnated activated carbon are still the best technology presently available for achieving this level of Hg control in mixed waste off-gas systems.

Using the off-gas technologies described above, some innovative mixed waste off-gas systems can be configured that are simpler, and might be more reliable, have lower technical risk, and lower costs than some current designs.

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